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PHYS 362 HW 11

## Problem 1

a.) $W_{by}$ for process 2 is greater than $W_{by}$ for process 1 because the area under the curve for $W_{by}$ process 2 is greater than that of $W_{by}$ for process 1.

b.) Because there is no change in energy for process 1 but there is a change in energy for process 2 with negative work, the change in Helmholtz free energy for process 2 is greater than that of process 1.

c.) Heat is transfered in a way that is not possible $\therefore$ this is not possible

## Problem 2

a.) $H = E + PV$ : $H_i = E_i + PV_i$ , $H_F = E_F + PV_F$ : $\Delta H = H_F - H_i$ $\quad PV = NKT$

$\Delta H = E_F - E_i + P(V_F - V_i) = \Delta E + P\Delta V$ : $\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + \cancel{P}\frac{\Delta(NKT)}{\cancel{P}} = \Delta E + KT\Delta N$ : $\Delta H = \Delta E + KT\Delta N$ : $\Delta N = 1\,mol - 3\,mol = -2\,mol$

$\Delta E = \Delta H - KT\Delta N = -890{,}000\ \frac{J}{mol}(1\,mol) - 1.38\times10^{-23}\ \frac{J}{K}(298K)(-2\cdot mol\cdot 6.02\times10^{23}\ J/mol)$

$= -890{,}000\ J - 4{,}951\ J = -894{,}951\ J$

$\boxed{\Delta E = -894{,}951\ J}$

b.) $\Delta S = S_F - S_i = (213.74\ \frac{J}{Kmol} + 2\cdot 69.91\ \frac{J}{Kmol}) - (186.3\ \frac{J}{Kmol} + 2\cdot 205.1\ \frac{J}{Kmol}) = -243\ \frac{J}{Kmol}$

$\boxed{\Delta S < 0 : \text{this is possible because we are not accounting for the } \Delta S \text{ of the atmosphere.}}$

c.) $G = H - TS$ : $\Delta G = \Delta H - T\Delta S = -890{,}000\ \frac{J}{mol} - 298K\cdot(-243\ \frac{J}{Kmol}) = -817{,}586\ \frac{J}{mol}$

$\Delta G = -817{,}586\ \frac{J}{mol}$ : $\Delta G \leq W_{non\text{-}mech}$ $\therefore$ $W_{non\text{-}mech} \geq -817{,}886\ J$

$\boxed{W_{non\text{-}mech} \geq -817{,}586\ J}$

This value is smaller in magnitude. This is necessary because we transfer energy in the form of heat during this process.

d.) $P = 1\,kW = 1{,}000\ W = 1{,}000\ \frac{J}{s}$ : $|\Delta G| = 817{,}586\ \frac{J}{mol}$

$P = |\Delta G|$ : $1000\ \frac{\cancel{J}}{\cancel{s}} = 817{,}586\ \frac{\cancel{J}}{mol}$ : $\frac{1000}{817{,}586}\ \frac{mol}{s}\ \frac{(3600s)}{(1hr)} = 4.403\ \frac{mol}{hr}$

$\boxed{4.403\ \frac{mol}{hr}}$

## Problem 3

a.) $G = E - TS + PV$ : T & V constant : $dE = Tds - P\,dV \rightsquigarrow \Delta E = T\Delta S - P\Delta V$ : $\Delta E - T\Delta S = -P\Delta V$

$G_i = E_i - TS_i + PV_i$ , $G_f = E_f - TS_f + PV_f$ : $\Delta G = G_f - G_i = (E_f - E_i) - T(S_f - S_i) + P(V_f - V_i) = \Delta E - T\Delta S + P\Delta V$

$\Delta G = \Delta E - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V \quad \therefore \quad \Delta S_{sys} = \frac{1}{T}[Q + W - \Delta G + P\Delta V]$

$\Delta S \geq 0 \quad \therefore \quad \Delta S_{res} + \Delta S_{sys} \geq 0 \quad -\frac{Q}{T} + \frac{1}{T}[Q + W - \Delta G + P\Delta V] \geq 0$

$-Q + Q + W - \Delta G + P\Delta V \geq 0$ : $W \geq \Delta G - P\Delta V$

$$\Delta G - P\Delta V \leq W$$

b.) $\Delta G - P\Delta V \leq W_{nm}$: $W_{nm} \rightarrow -P\Delta V \quad \therefore \quad \Delta G \leq P\Delta V - P\Delta V \leq 0$

$$\Delta G \leq 0$$

c.) $G = E - TS + PV$ : $H = E + PV \quad \therefore \quad G = H - TS$

$$G = H - TS$$

d.) $\Delta G = \Delta H - T\Delta S$

$\Delta G = (-699{,}650\ J/mol - (-393{,}510\ J/mol - 285{,}830\ J/mol)) - (298\ K)(187.4\ J/K\,mol - (213.74\ J/K\,mol + 69.91\ J/K\,mol))$

$\Delta G = 8{,}373\ \frac{J}{mol}$ : This is not spontaneous because $\Delta G > 0$

$\Delta G = 0$ : $T = \dfrac{(-699{,}650\ J/mol - (-393{,}510\ J/mol - 285{,}830\ J/mol))}{(187.4\ J/K\,mol - (213.74\ J/K\,mol + 69.91\ J/K\,mol))} = 211\ K$

For this to be spontaneous, $T = 211\ K$

$$\Delta G = 8{,}373\ \frac{J}{mol}\text{, not spontaneous, } T = 211\ K$$